

## MOLECULAR SIEVE CIT-6

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3 1998.

## **BACKGROUND OF THE INVENTION**

### Field of the Invention

6 The present invention relates to new crystalline molecular sieve CIT-6, a method for  
7 preparing CIT-6 using a tetraethylammonium cation templating agent, a method of using  
8 CIT-6 as a precursor for making other crystalline molecular sieves, and processes employing  
9 CIT-6 as a catalyst.

## **State of the Art**

Because of their unique sieving characteristics, as well as their catalytic properties, crystalline molecular sieves are especially useful in applications such as hydrocarbon conversion, gas drying and separation. Although many different crystalline molecular sieves have been disclosed, there is a continuing need for new molecular sieves with desirable properties for gas separation and drying, hydrocarbon and chemical conversions, and other applications. New molecular sieves may contain novel internal pore architectures, providing enhanced selectivities in these processes.

## SUMMARY OF THE INVENTION

19 The present invention is directed to a crystalline molecular sieve with unique  
20 properties, referred to herein as "molecular sieve CIT-6" or simply "CIT-6". When the CIT-  
21 6 contains a metal (or non-silicon) oxide, such as aluminum oxide, boron oxide, titanium  
22 oxide or iron oxide, it is referred to as "catalytically active" CIT-6.

23 The CIT-6 can be made in two forms. The first contains silicon oxide, zinc oxide  
24 and optional metal (or non-silicon) oxides (such as aluminum oxide), wherein the zinc is in  
25 the crystal framework of the CIT-6. This form of CIT-6 is referred to herein as "Zn-CIT-6".

Another form of CIT-6 is where the molecular sieve is composed only of silicon oxide. This form of CIT-6 is referred to herein as "all-Si CIT-6".

28 Zn-CIT-6 and all-Si CIT-6 each have the topology of zeolite beta.

29 In accordance with this invention, there is provided a molecular sieve comprising an  
30 oxide of silicon and an oxide of zinc and having the framework topology of zeolite beta,  
31 wherein the molecular sieve contains zinc in its crystal framework.

32 The present invention further provides such a molecular sieve having the topology of

1 zeolite beta, and having a composition, as synthesized and in the anhydrous state, in terms  
2 of mole ratios as follows:

3                   SiO<sub>2</sub>/ZnO     10-100  
4                   M/SiO<sub>2</sub>       0.01-0.1  
5                   Q/SiO<sub>2</sub>       0.07-0.14

6 wherein M is lithium or a mixture of lithium and another alkali metal, and Q comprises a  
7 tetraethylammonium cation, wherein the molecular sieve contains zinc in its crystal  
8 framework.

9                  Also in accordance with this invention there is provided a molecular sieve  
10 comprising silicon oxide, zinc oxide, and an oxide selected from aluminum oxide, boron  
11 oxide, gallium oxide, iron oxide, titanium oxide, vanadium oxide, zirconium oxide, tin  
12 oxide or mixtures thereof and having the framework topology of zeolite beta, wherein the  
13 molecular sieve contains zinc in its crystal framework.

14                  The present invention also provides such a molecular sieve having the topology of  
15 zeolite beta, and having a composition, as synthesized and in the anhydrous state, in terms  
16 of mole ratios as follows:

17                   SiO<sub>2</sub>/ZnO     10-100  
18                   SiO<sub>2</sub>/W       30-250  
19                   M/SiO<sub>2</sub>       0.01-0.1  
20                   Q/SiO<sub>2</sub>       0.07-0.14

21 wherein W is an oxide of aluminum, boron, gallium, vanadium, iron, titanium or mixtures  
22 thereof M is lithium or a mixture of lithium and another alkali metal, and Q comprises a  
23 tetraethylammonium cation, wherein the molecular sieve contains zinc in its crystal  
24 framework.

25                  Also provided in accordance with the present invention is a method of preparing a  
26 crystalline material comprising an oxide of silicon and an oxide of zinc and having the  
27 framework topology of zeolite beta, wherein the molecular sieve contains zinc in its crystal  
28 framework, said method comprising contacting in admixture under crystallization conditions  
29 sources of said oxides, a source of lithium or a mixture of lithium and another alkali metal  
30 and a templating agent comprising a tetraethylammonium cation.

31                  The present invention also provides a method of preparing a crystalline material  
32 comprising an oxide of silicon, an oxide of zinc and an oxide selected from aluminum

1 oxide, boron oxide, gallium oxide, vanadium oxide, iron oxide, titanium oxide or mixtures  
2 thereof and having the framework topology of zeolite beta, wherein the molecular sieve  
3 contains zinc in its crystal framework, said method comprising contacting in admixture  
4 under crystallization conditions sources of said oxides, a source of lithium or a mixture of  
5 lithium and another alkali metal and a templating agent comprising a tetraethylammonium  
6 cation.

7 Further provided by the present invention is a method of removing a  
8 tetraethylammonium organic template from the pores of a molecular sieve, said method  
9 comprising contacting the molecular sieve with acetic acid, or a mixture of acetic acid and  
10 pyridine at elevated temperature for a time sufficient to remove essentially all of the  
11 tetraethylammonium organic template from the molecular sieve. In a preferred embodiment,  
12 the molecular sieve has the topology of zeolite beta.

13 The present invention further provides a method of removing an organic template  
14 from the pores of a molecular sieve and at the same time removing zinc atoms from the  
15 framework of the molecular sieve, wherein the molecular sieve comprises an oxide of  
16 silicon, an oxide of zinc and, optionally an oxide selected from aluminum oxide, boron  
17 oxide, gallium oxide, vanadium oxide, iron oxide, titanium oxide or mixtures thereof, and  
18 has the framework topology of zeolite beta, said method comprising contacting the  
19 molecular sieve with acetic acid or a mixture of acetic acid and pyridine at elevated  
20 temperature for a time sufficient to remove essentially all of the organic template and zinc  
21 from the molecular sieve. The present invention also provides the product of this method.

22 Also provided by the present invention is a method of making a crystalline material  
23 comprising (1) contacting in admixture under crystallization conditions a source of silicon  
24 oxide, a source of zinc oxide, a source of lithium or a mixture of lithium and another alkali  
25 metal and a templating agent comprising a tetraethylammonium cation until a crystalline  
26 material comprised of oxides of silicon and zinc and having the topology of zeolite beta is  
27 formed, (2) contacting the crystals with acetic acid or a mixture of acetic acid and pyridine  
28 at an elevated temperature of about 60°C or less for a time sufficient to remove essentially  
29 all of the organic template and zinc from the crystals, and (3) contacting the crystals with a  
30 solution containing a source of aluminum, boron, gallium, iron, vanadium, titanium,  
31 zirconium, tin or mixtures thereof. The present invention also provides the product of this  
32 method.

1        This invention also provides a crystalline molecular sieve having the topology of  
2        zeolite beta, a crystal size of less than one micron and a water adsorption capacity of less  
3        than 0.05 g/g of molecular sieve.

4        Further provided by the present invention is a crystalline silicate molecular sieve  
5        having the topology of zeolite beta, a crystal size of less than one micron and a water  
6        adsorption capacity of less than 0.05 g/g of molecular sieve.

7        In addition, the present invention provides a method of preparing a crystalline  
8        material having the topology of zeolite beta comprising impregnating a silica-containing  
9        mesoporous material with an aqueous solution comprising tetraethylammonium cation in an  
10      amount sufficient to form a crystalline product having the topology of zeolite beta, and  
11      wherein the water to mesoporous material molar ratio is from about 0.5 to about 2, and  
12      subjecting the impregnated mesoporous material to crystallizing conditions of heat and  
13      pressure for a time sufficient to form crystals of a material having the topology of zeolite  
14      beta.

15       The present invention additionally provides a process for converting hydrocarbons  
16      comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with  
17      a catalyst comprising a catalytically active molecular sieve comprising silicon oxide, zinc  
18      oxide, and an oxide selected from aluminum oxide, boron oxide, gallium oxide, iron oxide,  
19      zirconium oxide, tin oxide or mixtures thereof and having the framework topology of zeolite  
20      beta, wherein the molecular sieve contains zinc in its crystal framework. The molecular  
21      sieve may be predominantly in the hydrogen form, partially acidic or substantially free of  
22      acidity, depending on the process.

23       Further provided by the present invention is a hydrocracking process comprising  
24      contacting a hydrocarbon feedstock under hydrocracking conditions with a catalyst  
25      comprising the catalytically active molecular sieve of this invention, preferably  
26      predominantly in the hydrogen form.

27       This invention also includes a dewaxing process comprising contacting a  
28      hydrocarbon feedstock under dewaxing conditions with a catalyst comprising the  
29      catalytically active molecular sieve of this invention, preferably predominantly in the  
30      hydrogen form.

31       The present invention also includes a process for improving the viscosity index of a  
32      dewaxed product of waxy hydrocarbon feeds comprising contacting the waxy hydrocarbon

1 feed under isomerization dewaxing conditions with a catalyst comprising the catalytically  
2 active molecular sieve of this invention, preferably predominantly in the hydrogen form.

3 The present invention further includes a process for producing a C<sub>20+</sub> lube oil from a  
4 C<sub>20+</sub> olefin feed comprising isomerizing said olefin feed under isomerization conditions over  
5 a catalyst comprising at least one Group VIII metal and the catalytically active molecular  
6 sieve of this invention. The molecular sieve may be predominantly in the hydrogen form.

7 In accordance with this invention, there is also provided a process for catalytically  
8 dewaxing a hydrocarbon oil feedstock boiling above about 350°F and containing straight  
9 chain and slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil  
10 feedstock in the presence of added hydrogen gas at a hydrogen pressure of about  
11 15-3000 psi with a catalyst comprising at least one Group VIII metal and the catalytically  
12 active molecular sieve of this invention, preferably predominantly in the hydrogen form.

13 The catalyst may be a layered catalyst comprising a first layer comprising at least one  
14 Group VIII metal and the catalytically active molecular sieve of this invention, and a  
15 second layer comprising an aluminosilicate zeolite which is more shape selective than the  
16 catalytically active molecular sieve of said first layer.

17 Also included in the present invention is a process for preparing a lubricating oil  
18 which comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to  
19 obtain an effluent comprising a hydrocracked oil, and catalytically dewaxing said effluent  
20 comprising hydrocracked oil at a temperature of at least about 400°F and at a pressure of  
21 from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a catalyst  
22 comprising at least one Group VIII metal and the catalytically active molecular sieve of this  
23 invention. The molecular sieve may be predominantly in the hydrogen form.

24 Further included in this invention is a process for isomerization dewaxing a raffinate  
25 comprising contacting said raffinate in the presence of added hydrogen with a catalyst  
26 comprising at least one Group VIII metal and the catalytically active molecular sieve of this  
27 invention. The raffinate may be bright stock, and the molecular sieve may be predominantly  
28 in the hydrogen form.

29 Also included in this invention is a process for increasing the octane of a  
30 hydrocarbon feedstock to produce a product having an increased aromatics content  
31 comprising contacting a hydrocarbonaceous feedstock which comprises normal and slightly  
32 branched hydrocarbons having a boiling range above about 40°C and less than about 200°C,

1 under aromatic conversion conditions with a catalyst comprising the catalytically active  
2 molecular sieve of this invention made substantially free of acidity by neutralizing said  
3 molecular sieve with a basic metal. Also provided in this invention is such a process  
4 wherein the molecular sieve contains a Group VIII metal component.

5 Also provided by the present invention is a catalytic cracking process comprising  
6 contacting a hydrocarbon feedstock in a reaction zone under catalytic cracking conditions in  
7 the absence of added hydrogen with a catalyst comprising the catalytically active molecular  
8 sieve of this invention, preferably predominantly in the hydrogen form. Also included in  
9 this invention is such a catalytic cracking process wherein the catalyst additionally  
10 comprises a large pore crystalline cracking component.

11 Also provided by the present invention is a process for alkylating an aromatic  
12 hydrocarbon which comprises contacting under alkylation conditions at least a molar excess  
13 of an aromatic hydrocarbon with a C<sub>2</sub> to C<sub>20</sub> olefin under at least partial liquid phase  
14 conditions and in the presence of a catalyst comprising the catalytically active molecular  
15 sieve of this invention, preferably predominantly in the hydrogen form. The olefin may be a  
16 C<sub>2</sub> to C<sub>4</sub> olefin, and the aromatic hydrocarbon and olefin may be present in a molar ratio of  
17 about 4:1 to about 20:1, respectively. The aromatic hydrocarbon may be selected from the  
18 group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

19 Further provided in accordance with this invention is a process for transalkylating an  
20 aromatic hydrocarbon which comprises contacting under transalkylating conditions an  
21 aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial liquid  
22 phase conditions and in the presence of a catalyst comprising the catalytically active  
23 molecular sieve of this invention, preferably predominantly in the hydrogen form. The  
24 aromatic hydrocarbon and the polyalkyl aromatic hydrocarbon may be present in a molar  
25 ratio of from about 1:1 to about 25:1, respectively. The aromatic hydrocarbon may be  
26 selected from the group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures  
27 thereof, and the polyalkyl aromatic hydrocarbon may be a dialkylbenzene.

28 Further provided by this invention is a process to convert paraffins to aromatics  
29 which comprises contacting paraffins under conditions which cause paraffins to convert to  
30 aromatics with a catalyst comprising the catalytically active molecular sieve of this  
31 invention, said catalyst comprising gallium, zinc, or a compound of gallium or zinc.

32 In accordance with this invention there is also provided a process for isomerizing

1 olefins comprising contacting said olefin under conditions which cause isomerization of the  
2 olefin with a catalyst comprising the catalytically active molecular sieve of this invention.

3       Further provided in accordance with this invention is a process for isomerizing an  
4 isomerization feed comprising an aromatic C<sub>8</sub> stream of xylene isomers or mixtures of  
5 xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-, meta-  
6 and para-xlenes is obtained, said process comprising contacting said feed under  
7 isomerization conditions with a catalyst comprising the catalytically active molecular sieve  
8 of this invention.

9       The present invention further provides a process for oligomerizing olefins  
10 comprising contacting an olefin feed under oligomerization conditions with a catalyst  
11 comprising the catalytically active molecular sieve of this invention.

12       This invention also provides a process for converting lower alcohols and other  
13 oxygenated hydrocarbons comprising contacting said lower alcohol or other oxygenated  
14 hydrocarbon with a catalyst comprising the catalytically active molecular sieve of this  
15 invention under conditions to produce liquid products.

16       Also provided by the present invention is an improved process for the reduction of  
17 oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process  
18 comprises contacting the gas stream with a molecular sieve, the improvement comprising  
19 using as the molecular sieve, the molecular sieve of this invention. The molecular sieve  
20 may contain a metal or metal ions (such as cobalt, copper or mixtures thereof) capable of  
21 catalyzing the reduction of the oxides of nitrogen, and may be conducted in the presence of  
22 a stoichiometric excess of oxygen. In a preferred embodiment, the gas stream is the exhaust  
23 stream of an internal combustion engine.

24       Further provided by the present invention is a method of removing liquid organic  
25 compounds from a mixture of liquid organic compounds and water, comprising contacting  
26 the mixture with an all-silica molecular sieve having the framework topology of zeolite beta,  
27 a crystal size less than one micron and a water adsorption capacity of less than 0.05 g/g of  
28 molecular sieve.

29       The present invention further provides a method of removing liquid organic  
30 compounds from a mixture of liquid organic compounds and water, comprising contacting  
31 the mixture with a molecular sieve comprising an oxide of silicon, an oxide of zinc and,  
32 optionally, an oxide selected from aluminum oxide, boron oxide, gallium oxide, iron oxide,

1 vanadium oxide, titanium oxide, zirconium oxide, tin oxide and mixtures thereof, and  
2 having the framework topology of zeolite beta, wherein the molecular sieve contains zinc in  
3 its crystal framework.

4 BRIEF DESCRIPTION OF THE DRAWINGS

5 Figures 1 and 2 show the results of water adsorption isotherms at 25°C of the molecular  
6 sieves of this invention and beta zeolite.

7 DETAILED DESCRIPTION OF THE INVENTION

8 In preparing CIT-6 molecular sieves, a tetraethylammonium cation ("TEA") is used  
9 as a crystallization template (-also known as a structure directing agent, or SDA). The anion  
10 associated with the cation may be any anion which is not detrimental to the formation of the  
11 molecular sieve. Representative anions include halogen, e.g., fluoride, chloride, bromide  
12 and iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like.  
13 Hydroxide is the most preferred anion.

14 In general, Zn-CIT-6 is prepared by contacting an active source of silicon oxide, an  
15 active source of zinc oxide, an active source of lithium or mixture of lithium and another  
16 alkali metal with the TEA templating agent.

17 Zn-CIT-6 is prepared from a reaction mixture having the following composition:



19 where M is lithium or a mixture of lithium and another alkali metal, b = 0.05-0.1; c = 0.55-  
20 0.7; a = 0.03-0.05; d = 30-40. It is believed the concentrations of Li<sup>+</sup>, Zn<sup>2+</sup> and TEAOH are  
21 critical to the formation of Zn-CIT-6.

22 When it is desired to prepare Zn-CIT-6 containing zinc oxide in combination with  
23 another metal oxide, such as aluminum oxide, a reaction mixture having the following  
24 composition:



26 where M is lithium or a mixture of lithium and another alkali metal, W is an oxide of  
27 aluminum, boron, gallium, vanadium, iron, titanium or mixtures thereof; b, c, a and d are as  
28 defined above and e = 0.005-0.1.

1       In practice, Zn-CIT-6 is prepared by a process comprising:

- 2             (a) preparing an aqueous solution containing sources of silicon oxide, zinc oxide,  
3                   lithium or a mixture of lithium and another alkali metal, TEA having an anionic  
4                   counterion which is not detrimental to the formation of Zn-CIT-6, and, optionally, an  
5                   oxide selected from aluminum oxide, boron oxide, gallium oxide, vanadium oxide,  
6                   iron oxide, titanium oxide or mixtures thereof;
- 7             (b) maintaining the aqueous solution under conditions sufficient to form crystals  
8                   of Zn-CIT-6; and
- 9             (c) recovering the crystals of Zn-CIT-6.

10      The aqueous solution prepared in step (a) should be a clear solution. In some cases, heating  
11     a reaction mixture that is a white, cloudy mixture at room temperature will convert the  
12     mixture to a clear solution from which Zn-CIT-6 will form.

13      It has been discovered that higher amounts of TEA and lower reaction temperatures  
14     favor the formation of Zn-CIT-6.

15      Typical sources of silicon oxide include silicates, silica hydrogel, silicic acid, fumed  
16     silica, colloidal silica, tetra-alkyl orthosilicates, and silica hydroxides. Typical sources of  
17     zinc oxide include water-soluble zinc salts, such as zinc acetate. Typical sources of  
18     aluminum oxide for the reaction mixture include aluminates, alumina, aluminum colloids,  
19     aluminum oxide coated on silica sol, and hydrated alumina gels such as Al(OH)<sub>3</sub>. Sources  
20     of boron, gallium, vanadium, iron and titanium compounds analogous to those listed for  
21     silicon and aluminum, and are known in the art.

22      Lithium or a mixture of lithium and another alkali metal is added to the reaction  
23     mixture. A variety of sources can be used, such as alkali metal hydroxides and alkali metal  
24     carbonates, with lithium hydroxide being particularly preferred. The lithium cation may be  
25     part of the as-synthesized crystalline oxide material, in order to balance valence electron  
26     charges therein. Other alkali metals which can be used in combination with the lithium  
27     include sodium and potassium, with the hydroxides being preferred, provided that lithium is  
28     the predominant alkali metal in the combination. The alkali metal (i.e., lithium or mixture  
29     of lithium and another alkali metal) may be employed in an amount of from about 0.05 to  
30     about 0.1 mole of alkali metal per mole of silica.

31      The reaction mixture is maintained at an elevated temperature until the crystals of  
32     the Zn-CIT-6 molecular sieve are formed. The hydrothermal crystallization is usually

1 conducted under autogenous pressure, at about 100°C to less than about 150°C. It has been  
2 discovered that higher reaction temperatures, e.g., 150°C and higher, favor the formation of  
3 a molecular sieve having the topology of zeolite VPI-8 rather than the desired molecular  
4 sieve with the topology of zeolite beta. Preferably, the reaction temperature should be about  
5 135°C to 150°C.

6 The crystallization period is typically greater than 1 day to less than 7 days. The Zn-  
7 CIT-6 crystals should be recovered from the reaction mixture as soon as they form, since it  
8 has been discovered that under some circumstances if they remain in the reaction mixture  
9 for too long after formation, they can convert to a molecular sieve having the topology of  
10 VPI-8.

11 During the hydrothermal crystallization step, the Zn-CIT-6 crystals can be allowed  
12 to nucleate spontaneously from the reaction mixture. The use of Zn-CIT-6 crystals as seed  
13 material can be advantageous in decreasing the time necessary for complete crystallization  
14 to occur. In addition, seeding can lead to an increased purity of the product obtained by  
15 promoting the nucleation and/or formation of Zn-CIT-6 over any undesired phases. When  
16 used as seeds, Zn-CIT-6 crystals are added in an amount between 0.1 and 10% of the weight  
17 of silica used in the reaction mixture.

18 Once the molecular sieve crystals have formed, the solid product is separated from  
19 the reaction mixture by standard mechanical separation techniques such as filtration. The  
20 crystals are water-washed and then dried, e.g., at 90°C to 150°C for from 8 to 24 hours, to  
21 obtain the as-synthesized Zn-CIT-6 molecular sieve crystals. The drying step can be  
22 performed at atmospheric pressure or under vacuum.

23 Zn-CIT-6 has a composition, as synthesized and in the anhydrous state, in terms of  
24 mole ratios, shown in Table B below.

25 TABLE B

26 As-Synthesized Zn-CIT-6

27	SiO <sub>2</sub> /ZnO	10-100
28	M/SiO <sub>2</sub>	0.01-0.1
29	Q/SiO <sub>2</sub>	0.07-0.14

30 where M and Q are as defined above.

31 Zn-CIT-6 can also have a composition, as synthesized and in the anhydrous state, in  
32 terms of mole ratios, shown in Table C below.

TABLE C  
As-Synthesized Zn-CIT-6

$\text{SiO}_2/\text{ZnO}$	10-100
$\text{SiO}_2/\text{W}$	30-250
$\text{M}/\text{SiO}_2$	0.01-0.1
$\text{Q}/\text{SiO}_2$	0.07-0.14

where W, M and Q are as defined above.

Solid state  $^{29}\text{Si}$  NMR analysis and acidity measurements have shown that at least part of the zinc is in the framework of the Zn-CIT-6 crystals. Indeed, in one embodiment, the Zn-CIT-6 crystal framework contains only silicon, zinc and oxygen atoms, i.e., there are no other metals in this form of Zn-CIT-6.

Once the Zn-CIT-6 crystals have been formed and recovered, the organic template should be removed. This is typically done by calcining the crystals at high temperature until the organic template is removed. However, it has been discovered that calcination can be avoided by extracting the organic template from the molecular sieve. This extraction technique has advantages over calcination. For example, no calcination equipment is needed. Also, the organic template is not destroyed by the extraction, so it may be possible to recycle it, thereby reducing the cost of making the molecular sieve.

The organic template can be removed by contacting the Zn-CIT-6 crystals with acetic acid or a mixture of acetic acid and pyridine at a temperature of about 80°C to about 135°C for a period sufficient to remove essentially all of the organic template from the crystals (typically about two days). At the same time, the zinc is removed from the crystals, and they convert to all-Si CIT-6, i.e., an all-silica crystal having the framework topology of zeolite beta. As shown by water adsorption isotherms, all-Si CIT-6 is highly hydrophobic. <sup>29</sup>Si NMR analysis further shows that the crystal lattice has virtually no defects.

26 It has quite surprisingly been found that CIT-6 prepared as described above, i.e., the  
27 CIT-6 is prepared and then contacted with acetic acid or a mixture of acetic acid and  
28 pyridine at a temperature of about 80°C to about 135°C (referred to herein as "extraction"),  
29 is highly hydrophobic. This is in marked contrast to CIT-6 or beta zeolite in which the  
30 organic template has been removed by calcination.

This phenomenon is illustrated in the Figure 1. Five water adsorption isotherms are shown for the following materials:

- 1           (a)     All-Si-CIT-6 prepared by extraction at 135°C.  
2           (b)     Zn-CIT-6 prepared using calcination  
3           (c)     Silicoalumino-CIT-6 extracted at 60°C followed by insertion of  
4                       aluminum  
5           (d)     Silicoalumino-CIT-6 prepared using aluminum oxide in the reaction  
6                       mixture with the product extracted at 135°C  
7           (e)     Calcined all-silica beta zeolite

8       The data indicate that the extracted aluminum-containing CIT-6 (sample d) is more  
9       hydrophobic than the sample prepared via aluminum insertion (sample c) and far more  
10      hydrophobic than the calcined zeolite beta (sample e). Calcined Zn-CIT-6 (sample b)  
11      likewise is far more hydrophobic than calcined zeolite beta, with extracted all-Si-CIT-6  
12      (sample a) exhibiting the highest degree of hydrophobicity.

13       Alternatively, the extraction or removal of the organic template from Zn-CIT-6 can  
14      be accomplished by contacting the Zn-CIT-6 crystal with acetic acid or a mixture of acetic  
15      acid and pyridine at an elevated temperature of about 60°C or less for a period sufficient to  
16      remove essentially all of the organic template from the crystals.

17       It has also been found that this latter extraction technique also removes some or all  
18      of the zinc atoms from the crystal framework. However, in this case the resultant molecular  
19      sieve contains internal silanol groups and other metals (or non-silicon atoms), such as  
20      aluminum, boron, gallium, vanadium, iron, titanium, zirconium, tin or mixtures thereof can  
21      be inserted into the crystal framework, replacing the zinc.

22       The metal can be inserted into the crystal framework by contacting the molecular  
23      sieve with a solution containing a source, such as a salt, of the desired metal. Although a  
24      wide variety of sources can be employed, chlorides and other halides, acetates, nitrates, and  
25      sulfates are particularly preferred. The preferred metals (or non-silicon atoms) are  
26      aluminum, boron, gallium, iron, titanium, vanadium, zirconium, tin, zinc and mixtures  
27      thereof. Representative techniques for inserting the metal are disclosed in a wide variety of  
28      patents including U. S. Patent No. 3,140,249, issued July 7, 1964 to Plank et al.; U. S.  
29      Patent No. 3,140,251, issued on July 7, 1964 to Plank et al.; and U. S. Patent No. 3,140,253,  
30      issued on July 7, 1964 to Plank et al., each of which is incorporated by reference herein. By  
31      way of example, aluminum can be inserted into the molecular sieve in place of some or all  
32      of the zinc by extracting the zinc (at about 60°C) as described above, and then contacting the

1 molecular sieve with an aluminum nitrate solution in about a 1 : 2 : 50 weight ratio of sieve :  
2 aluminum nitrate : water at about 80°C for about one day.

3 As an alternative to making Zn-CIT-6, extracting the zinc and inserting, e.g.,  
4 aluminum, an aluminosilicate can be made directly by synthesizing aluminozincosilicate  
5 CIT-6 as described above and in Example 27, and then extracting the zinc at the higher  
6 extraction temperature (135°C). This removes the zinc from the CIT-6 and leaves an  
7 aluminosilicate molecular sieve with the topology of zeolite beta.  $^{27}\text{Al}$  NMR analysis of  
8 aluminosilicates made in this manner shows that the aluminum remains in the crystal  
9 framework.

10 All-Si CIT-6 can be made by preparing Zn-CIT-6 as described above, followed by  
11 extraction of the zinc. It has surprisingly been found that all-Si CIT-6 made by this method  
12 has a much lower water adsorption capacity than all-silica zeolite beta made by traditional  
13 methods. The all-Si CIT-6 made by this method also has a crystal size of less than about  
14 one micron, whereas all-silica zeolite beta made by traditional method has a crystal size of  
15 greater than one micron, e.g., on the order of five microns. Furthermore, the all-Si CIT-6  
16 made by this method has essentially no defect (i.e., Si-OH instead of Si-O-Si) sites, whereas  
17 all-silica zeolite beta made by traditional methods does contain defect sites that adsorb  
18 water.

19 A series of silica-containing mesoporous materials denoted M41S have been  
20 reported. These materials have been further classified, e.g., MCM-41 (hexagonal), MCM-  
21 48 (cubic) and others. These materials have uniform pores of 1.5 – 10 nm diameters, and  
22 are made by using a variety of surfactants as structure-directing agents. Non-silicon atom,  
23 e.g., Al, B, Ga, Ti, V, Zr, Fe, Mn, Sn, Zn, Cu and Nb, containing mesoporous materials have  
24 also been prepared.

25 The inorganic portion of MCM-41 resembles amorphous silicas rather than  
26 crystalline molecular sieves in terms of the local structure and bonding, but has many  
27 peculiar properties. It possesses uniformly sized mesopores with thin walls (around 10  
28 Angstroms) and shows hydrophobic adsorption behavior.

29 It has now been discovered that zeolites having the topology of zeolite beta, in either  
30 all-silica form or in a form containing silica and metal (or non-silicon) oxide(s), can be  
31 made using the inorganic portion of ordered, mesoporous materials as reagents. The  
32 mesoporous materials may be all-silica, or they may contain silica and metal (or non-

1 silicon) oxide(s), e.g., aluminum oxide. Examples of such mesoporous materials include,  
2 but are not limited to, MCM-41 and MCM-48.

3 The mesoporous materials are used in combination with tetraethylammonium cation  
4 organic templating agent, e.g., tetraethylammonium hydroxide (TEAOH). It has been found  
5 that, in order to assure the zeolite beta has essentially no defect sites, the reaction mixture  
6 containing the mesoporous material and TEAOH should be in the form of a "dry gel". The  
7 dry gel is made by impregnating the mesoporous material with an aqueous solution of  
8 TEAOH, allowing the resulting impregnated material to dry for about one day at room  
9 temperature. The thus-impregnated product should have a molar ratio of water to  
10 mesoporous material of about 0.5 to about 2, and contain sufficient TEAOH to cause  
11 formation of the beta structure. The impregnated material is then subject to crystallization  
12 conditions in an autoclave. The resulting crystalline product can either be calcined to  
13 remove the TEAOH, or it can be subjected to the extraction technique described above, thus  
14 assuring the product will be essentially defect-free.

15 If it is desired that the final product contain silicon oxide and a metal (or non-silicon)  
16 oxide, the mesoporous starting material can contain silicon oxide and the desired metal (or  
17 non-silicon) oxide. Metal oxides such as aluminum oxide, titanium oxide, vanadium oxide,  
18 zinc oxide, zirconium oxide, and magnesium oxide, as well as non-silicon oxides such as  
19 boron oxide, can be incorporated into the zeolite beta structure in this manner.

20 The molecular sieves made by either of these two techniques are highly  
21 hydrophobic. Figure 2 shows the results of water adsorption isotherms for calcined all-silica  
22 beta zeolite (line 1), all-Si CIT-6 made from MCM-41 and subjected to extraction rather  
23 than calcination (line 2), and Zn-CIT-6 made by extraction (line 3). As can be seen, the  
24 water adsorption capacities of both the all-Si CIT-6 and Zn-CIT-6 are substantially lower  
25 than that of calcined all-silica beta zeolite.

26 When used in a catalyst, the molecular sieve can be used in intimate combination  
27 with hydrogenating components, such as tungsten, vanadium, molybdenum, rhenium,  
28 nickel, cobalt, chromium, manganese, or a noble metal, such as palladium or platinum, for  
29 those applications in which a hydrogenation-dehydrogenation function is desired.

30 Metals may also be introduced into the molecular sieve by replacing some of the  
31 cations in the molecular sieve with metal cations via standard ion exchange techniques (see,  
32 for example, U.S. Patent Nos. 3,140,249 issued July 7, 1964 to Plank et al.; 3,140,251

1 issued July 7, 1964 to Plank et al.; and 3,140,253 issued July 7, 1964 to Plank et al.).  
2 Typical replacing cations can include metal cations, e.g., rare earth, Group IA, Group IIA  
3 and Group VIII metals, as well as their mixtures. Of the replacing metallic cations, cations  
4 of metals such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are  
5 particularly preferred.

6 The hydrogen, ammonium, and metal components can be ion-exchanged into the  
7 catalytically active CIT-6. The molecular sieve can also be impregnated with the metals, or,  
8 the metals can be physically and intimately admixed with the molecular sieve using standard  
9 methods known to the art.

10 Typical ion-exchange techniques involve contacting the synthetic molecular sieve  
11 with a solution containing a salt of the desired replacing cation or cations. Although a wide  
12 variety of salts can be employed, chlorides and other halides, acetates, nitrates, and sulfates  
13 are particularly preferred. The molecular sieve is usually calcined prior to the ion-exchange  
14 procedure to remove the organic matter present in the channels and on the surface, since this  
15 results in a more effective ion exchange. Representative ion exchange techniques are  
16 disclosed in a wide variety of patents including U.S. Patent Nos. 3,140,249 issued on July 7,  
17 1964 to Plank et al.; 3,140,251 issued on July 7, 1964 to Plank et al.; and 3,140,253 issued  
18 on July 7, 1964 to Plank et al.

19 Following contact with the salt solution of the desired replacing cation, the  
20 molecular sieve is typically washed with water and dried at temperatures ranging from 65°C  
21 to about 200°C. After washing, the molecular sieve can be calcined in air or inert gas at  
22 temperatures ranging from about 200°C to about 800°C for periods of time ranging from 1  
23 to 48 hours, or more, to produce a catalytically active product especially useful in  
24 hydrocarbon conversion processes.

25 Regardless of the cations present in the synthesized form of CIT-6, the spatial  
26 arrangement of the atoms which form the basic crystal lattice of the molecular sieve remains  
27 essentially unchanged.

28 Catalytically active CIT-6 can be formed into a wide variety of physical shapes.  
29 Generally speaking, the molecular sieve can be in the form of a powder, a granule, or a  
30 molded product, such as extrudate having a particle size sufficient to pass through a 2-mesh  
31 (Tyler) screen and be retained on a 400-mesh (Tyler) screen. In cases where the catalyst is  
32 molded, such as by extrusion with an organic binder, the molecular sieve can be extruded

1 before drying, or, dried or partially dried and then extruded.

Catalytically active CIT-6 can be composited with other materials resistant to the temperatures and other conditions employed in organic conversion processes. Such matrix materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and metal oxides. Examples of such materials and the manner in which they can be used are disclosed in U.S. Patent No. 4,910,006, issued May 20, 1990 to Zones et al., and U.S. Patent No. 5,316,753, issued May 31, 1994 to Nakagawa, both of which are incorporated by reference herein in their entirety.

## Hydrocarbon Conversion Processes

The catalytically active CIT-6 molecular sieves are useful in hydrocarbon conversion reactions. Hydrocarbon conversion reactions are chemical and catalytic processes in which carbon containing compounds are changed to different carbon containing compounds. Examples of hydrocarbon conversion reactions in which catalytically active CIT-6 is expected to be useful include hydrocracking, dewaxing, catalytic cracking and olefin and aromatics formation reactions. The catalysts are also expected to be useful in other petroleum refining and hydrocarbon conversion reactions such as polymerizing and oligomerizing olefinic or acetylenic compounds such as isobutylene and butene-1, reforming, isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and disproportionating aromatics (e.g., toluene) to provide mixtures of benzene, xylenes and higher methylbenzenes and oxidation reactions. Also included are rearrangement reactions to make various naphthalene derivatives. The catalytically active CIT-6 catalysts may have high selectivity, and under hydrocarbon conversion conditions can provide a high percentage of desired products relative to total products.

25 The catalytically active CIT-6 molecular sieves can be used in processing  
26 hydrocarbonaceous feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds  
27 and can be from many different sources, such as virgin petroleum fractions, recycle  
28 petroleum fractions, shale oil, liquefied coal, tar sand oil, synthetic paraffins from NAO,  
29 recycled plastic feedstocks and, in general, can be any carbon containing feedstock  
30 susceptible to zeolitic catalytic reactions. Depending on the type of processing the  
31 hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals, it can  
32 also have high or low nitrogen or sulfur impurities. It can be appreciated, however, that in

1 general processing will be more efficient (and the catalyst more active) the lower the metal,  
2 nitrogen, and sulfur content of the feedstock.

3 The conversion of hydrocarbonaceous feeds can take place in any convenient mode,  
4 for example, in fluidized bed, moving bed, or fixed bed reactors depending on the types of  
5 process desired. The formulation of the catalyst particles will vary depending on the  
6 conversion process and method of operation.

7 Other reactions which can be performed using the catalyst of this invention  
8 containing a metal, e.g., a Group VIII metal such platinum, include  
9 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization reactions.

10 Depending upon the type of reaction which is catalyzed, the molecular sieve may be  
11 predominantly in the hydrogen form, partially acidic or substantially free of acidity. As  
12 used herein, "predominantly in the hydrogen form" means that, after calcination, at least  
13 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

14 The following table indicates typical reaction conditions which may be employed  
15 when using catalysts comprising catalytically active CIT-6 in the hydrocarbon conversion  
16 reactions of this invention. Preferred conditions are indicated in parentheses.  
17

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar	0.1-30
Dewaxing	200-475 (250-450)	15-3000 psig (200-3000)	0.1-20 (0.2-10)
Aromatics formation	400-600 (480-550)	atm.-10 bar	0.1-15
Cat. cracking	127-885	subatm. <sup>1</sup> (atm.-5 atm.)	0.5-50
Oligomerization	232-649 <sup>2</sup> 10-232 <sup>4</sup> (27-204) <sup>4</sup>	0.1-50 atm. <sup>2,3</sup>	0.2-50 <sup>2</sup> 0.05-20 <sup>5</sup> (0.1-10) <sup>5</sup>
Paraffins to aromatics	100-700	0-1000 psig	0.5-40 <sup>5</sup>
Condensation of alcohols	260-538	0.5-1000 psig	0.5-50 <sup>5</sup>
Xylene isomerization	260-593 <sup>2</sup> (315-566) <sup>2</sup> 38-371 <sup>4</sup>	0.5-50 atm. <sup>2</sup> (1-5 atm) <sup>2</sup> 1-200 atm. <sup>4</sup>	0.1-100 <sup>5</sup> (0.5-50) <sup>5</sup> 0.5-50

18

19 <sup>1</sup> Several hundred atmospheres

20 <sup>2</sup> Gas phase reaction

### 1      <sup>3</sup> Hydrocarbon partial pressure

## 2 Liquid phase reaction

- 3 - <sup>5</sup> WHSV

4 Other reaction conditions and parameters are provided below.

## Hydrocracking

Using a catalyst which comprises catalytically active CIT-6, preferably predominantly in the hydrogen form, and a hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and other hydrocrackate charge stocks can be hydrocracked using the process conditions and catalyst components disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753.

11        The hydrocracking catalysts contain an effective amount of at least one  
12      hydrogenation component of the type commonly employed in hydrocracking catalysts. The  
13      hydrogenation component is generally selected from the group of hydrogenation catalysts  
14      consisting of one or more metals of Group VIB and Group VIII, including the salts,  
15      complexes and solutions containing such. The hydrogenation catalyst is preferably selected  
16      from the group of metals, salts and complexes thereof of the group consisting of at least one  
17      of platinum, palladium, rhodium, iridium, ruthenium and mixtures thereof or the group  
18      consisting of at least one of nickel, molybdenum, cobalt, tungsten, titanium, chromium and  
19      mixtures thereof. Reference to the catalytically active metal or metals is intended to  
20      encompass such metal or metals in the elemental state or in some form such as an oxide,  
21      sulfide, halide, carboxylate and the like. The hydrogenation catalyst is present in an  
22      effective amount to provide the hydrogenation function of the hydrocracking catalyst, and  
23      preferably in the range of from 0.05 to 25% by weight.

### Dewaxing

25           Catalytically active CIT-6, preferably predominantly in the hydrogen form, can be  
26   used to dewax hydrocarbonaceous feeds by selectively removing straight chain paraffins.  
27   Typically, the viscosity index of the dewaxed product is improved (compared to the waxy  
28   feed) when the waxy feed is contacted with catalytically active CIT-6 under isomerization  
29   dewaxing conditions.

The catalytic dewaxing conditions are dependent in large measure on the feed used and upon the desired pour point. Hydrogen is preferably present in the reaction zone during the catalytic dewaxing process. The hydrogen to feed ratio is typically between about 500

1 and about 30,000 SCF/bbl (standard cubic feet per barrel), preferably about 1000 to about  
2 20,000 SCF/bbl. Generally, hydrogen will be separated from the product and recycled to the  
3 reaction zone. Typical feedstocks include light gas oil, heavy gas oils and reduced crudes  
4 boiling above about 350°F.

5 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil feedstock  
6 boiling above about 350°F and containing straight chain and slightly branched chain  
7 hydrocarbons by contacting the hydrocarbon oil feedstock in the presence of added  
8 hydrogen gas at a hydrogen pressure of about 15-3000 psi with a catalyst comprising  
9 - catalytically active CIT-6 and at least one Group VIII metal.

10 The catalytically active CIT-6 hydrodewaxing catalyst may optionally contain a  
11 hydrogenation component of the type commonly employed in dewaxing catalysts. See the  
12 aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for examples of  
13 these hydrogenation components.

14 The hydrogenation component is present in an effective amount to provide an  
15 effective hydrodewaxing and hydroisomerization catalyst preferably in the range of from  
16 about 0.05 to 5% by weight. The catalyst may be run in such a mode to increase  
17 isodewaxing at the expense of cracking reactions.

18 The feed may be hydrocracked, followed by dewaxing. This type of two stage  
19 process and typical hydrocracking conditions are described in U.S. Patent No. 4,921,594,  
20 issued May 1, 1990 to Miller, which is incorporated herein by reference in its entirety.

21 Catalytically active CIT-6 may also be utilized as a dewaxing catalyst in the form of  
22 a layered catalyst. That is, the catalyst comprises a first layer comprising catalytically active  
23 molecular sieve CIT-6 and at least one Group VIII metal, and a second layer comprising an  
24 aluminosilicate zeolite which is more shape selective than catalytically active molecular  
25 sieve CIT-6. The use of layered catalysts is disclosed in U.S. Patent No. 5,149,421, issued  
26 September 22, 1992 to Miller, which is incorporated by reference herein in its entirety. The  
27 layering may also include a bed of catalytically active CIT-6 layered with a non-zeolitic  
28 component designed for either hydrocracking or hydrofinishing.

29 Catalytically active CIT-6 may also be used to dewax raffinates, including bright  
30 stock, under conditions such as those disclosed in U. S. Patent No. 4,181,598, issued  
31 January 1, 1980 to Gillespie et al., which is incorporated by reference herein in its entirety.

32 It is often desirable to use mild hydrogenation (sometimes referred to as

hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step can be performed either before or after the dewaxing step, and preferably after. Hydrofinishing is typically conducted at temperatures ranging from about 190°C to about 340°C at pressures from about 400 psig to about 3000 psig at space velocities (LHSV) between about 0.1 and 20 and a hydrogen recycle rate of about 400 to 1500 SCF/bbl. The hydrogenation catalyst employed must be active enough not only to hydrogenate the olefins, diolefins and color bodies which may be present, but also to reduce the aromatic content. Suitable hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated by reference herein in its entirety. The hydrofinishing step is beneficial in preparing an acceptably stable product (e.g., a lubricating oil) since dewaxed products prepared from hydrocracked stocks tend to be unstable to air and light and tend to form sludges spontaneously and quickly.

Lube oil may be prepared using catalytically active CIT-6. For example, a C<sub>20+</sub> lube oil may be made by isomerizing a C<sub>20+</sub> olefin feed over a catalyst comprising catalytically active CIT-6 in the hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically dewaxing the effluent at a temperature of at least about 400°F and at a pressure of from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a catalyst comprising catalytically active CIT-6 in the hydrogen form and at least one Group VIII metal.

#### Aromatics Formation

Catalytically active CIT-6 can be used to convert light straight run naphthas and similar mixtures to highly aromatic mixtures. Thus, normal and slightly branched chained hydrocarbons, preferably having a boiling range above about 40°C and less than about 200°C, can be converted to products having a substantial higher octane aromatics content by contacting the hydrocarbon feed with a catalyst comprising catalytically active CIT-6. It is also possible to convert heavier feeds into BTX or naphthalene derivatives of value using a catalyst comprising catalytically active CIT-6.

The conversion catalyst preferably contains a Group VIII metal compound to have sufficient activity for commercial use. By Group VIII metal compound as used herein is meant the metal itself or a compound thereof. The Group VIII noble metals and their compounds, platinum, palladium, and iridium, or combinations thereof can be used.

1 Rhenium or tin or a mixture thereof may also be used in conjunction with the Group VIII  
2 metal compound and preferably a noble metal compound. The most preferred metal is  
3 platinum. The amount of Group VIII metal present in the conversion catalyst should be  
4 within the normal range of use in reforming catalysts, from about 0.05 to 2.0 weight percent,  
5 preferably 0.2 to 0.8 weight percent.

6 It is critical to the selective production of aromatics in useful quantities that the  
7 conversion catalyst be substantially free of acidity, for example, by neutralizing the  
8 molecular sieve with a basic metal, e.g., alkali metal, compound. Methods for rendering the  
9 catalyst free of acidity are known in the art. See the aforementioned U.S. Patent  
10 No. 4,910,006 and U.S. Patent No. 5,316,753 for a description of such methods.

11 The preferred alkali metals are sodium, potassium, rubidium and cesium.

12 Catalytic Cracking

13 Hydrocarbon cracking stocks can be catalytically cracked in the absence of hydrogen  
14 using catalytically active CIT-6, preferably predominantly in the hydrogen form.

15 When catalytically active CIT-6 is used as a catalytic cracking catalyst in the  
16 absence of hydrogen, the catalyst may be employed in conjunction with traditional cracking  
17 catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking  
18 catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of these  
19 traditional cracking catalysts are disclosed in the aforementioned U.S. Patent No. 4,910,006  
20 and U.S. Patent No. 5,316,753. When a traditional cracking catalyst (TC) component is  
21 employed, the relative weight ratio of the TC to the catalytically active CIT-6 is generally  
22 between about 1:10 and about 500:1, desirably between about 1:10 and about 200:1,  
23 preferably between about 1:2 and about 50:1, and most preferably is between about 1:1 and  
24 about 20:1. The novel molecular sieve and/or the traditional cracking component may be  
25 further ion exchanged with rare earth ions to modify selectivity.

26 The cracking catalysts are typically employed with an inorganic oxide matrix  
27 component. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent  
28 No. 5,316,753 for examples of such matrix components.

29 Alkylation and Transalkylation

30 Catalytically active CIT-6 can be used in a process for the alkylation or  
31 transalkylation of an aromatic hydrocarbon. The process comprises contacting the aromatic  
32 hydrocarbon with a C<sub>2</sub> to C<sub>16</sub> olefin alkylating agent or a polyalkyl aromatic hydrocarbon

1 transalkylating agent, under at least partial liquid phase conditions, and in the presence of a  
2 catalyst comprising catalytically active CIT-6.

3       Catalytically active CIT-6 can also be used for removing benzene from gasoline by  
4 alkylating the benzene as described above and removing the alkylated product from the  
5 gasoline.

6       For high catalytic activity, the catalytically active CIT-6 molecular sieve should be  
7 predominantly in its hydrogen ion form. It is preferred that, after calcination, at least 80% of  
8 the cation sites are occupied by hydrogen ions and/or rare earth ions.

9       Examples of suitable aromatic hydrocarbon feedstocks which may be alkylated or  
10 transalkylated by the process of the invention include aromatic compounds such as benzene,  
11 toluene and xylene. The preferred aromatic hydrocarbon is benzene. There may be  
12 occasions where naphthalene derivatives may be desirable. Mixtures of aromatic  
13 hydrocarbons may also be employed.

14       Suitable olefins for the alkylation of the aromatic hydrocarbon are those containing 2  
15 to 20, preferably 2 to 4, carbon atoms, such as ethylene, propylene, butene-1, trans-butene-2  
16 and cis-butene-2, or mixtures thereof. There may be instances where pentenes are desirable.  
17 The preferred olefins are ethylene and propylene. Longer chain alpha olefins may be used as  
18 well.

19       When transalkylation is desired, the transalkylating agent is a polyalkyl aromatic  
20 hydrocarbon containing two or more alkyl groups that each may have from 2 to about  
21 4 carbon atoms. For example, suitable polyalkyl aromatic hydrocarbons include di-, tri- and  
22 tetra-alkyl aromatic hydrocarbons, such as diethylbenzene, triethylbenzene,  
23 diethylmethylbenzene (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene,  
24 dibutylbenzene, and the like. Preferred polyalkyl aromatic hydrocarbons are the dialkyl  
25 benzenes. A particularly preferred polyalkyl aromatic hydrocarbon is di-isopropylbenzene.

26       When alkylation is the process conducted, reaction conditions are as follows. The  
27 aromatic hydrocarbon feed should be present in stoichiometric excess. It is preferred that  
28 molar ratio of aromatics to olefins be greater than four-to-one to prevent rapid catalyst  
29 fouling. The reaction temperature may range from 100°F to 600°F, preferably 250°F to  
30 450°F. The reaction pressure should be sufficient to maintain at least a partial liquid phase  
31 in order to retard catalyst fouling. This is typically 50 psig to 1000 psig depending on the  
32 feedstock and reaction temperature. Contact time may range from 10 seconds to 10 hours,

1 but is usually from 5 minutes to an hour. The weight hourly space velocity (WHSV), in  
2 terms of grams (pounds) of aromatic hydrocarbon and olefin per gram (pound) of catalyst  
3 per hour, is generally within the range of about 0.5 to 50.

4 When transalkylation is the process conducted, the molar ratio of aromatic  
5 hydrocarbon will generally range from about 1:1 to 25:1, and preferably from about 2:1 to  
6 20:1. The reaction temperature may range from about 100°F to 600°F, but it is preferably  
7 about 250°F to 450°F. The reaction pressure should be sufficient to maintain at least a  
8 partial liquid phase, typically in the range of about 50 psig to 1000 psig, preferably 300 psig  
9 to 600 psig. The weight hourly space velocity will range from about 0.1 to 10. U.S. Patent  
10 No. 5,082,990 issued on January 21, 1992 to Hsieh, et al. describes such processes and is  
11 incorporated herein by reference.

#### Isomerization of Olefins

13 Catalytically active CIT-6 can be used to isomerize olefins. The feed stream is a  
14 hydrocarbon stream containing at least one C<sub>4-6</sub> olefin, preferably a C<sub>4-6</sub> normal olefin, more  
15 preferably normal butene. Normal butene as used in this specification means all forms of  
16 normal butene, e.g., 1-butene, cis-2-butene, and trans-2-butene. Typically, hydrocarbons  
17 other than normal butene or other C<sub>4-6</sub> normal olefins will be present in the feed stream.  
18 These other hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen, and  
19 inert gases.

20 The feed stream typically may be the effluent from a fluid catalytic cracking unit or a  
21 methyl-tert-butyl ether unit. A fluid catalytic cracking unit effluent typically contains about  
22 40-60 weight percent normal butenes. A methyl-tert-butyl ether unit effluent typically  
23 contains 40-100 weight percent normal butene. The feed stream preferably contains at least  
24 about 40 weight percent normal butene, more preferably at least about 65 weight percent  
25 normal butene. The terms iso-olefin and methyl branched iso-olefin may be used  
26 interchangeably in this specification.

27 The process is carried out under isomerization conditions. The hydrocarbon feed is  
28 contacted in a vapor phase with a catalyst comprising the catalytically active CIT-6. The  
29 process may be carried out generally at a temperature from about 625°F to about 950°F  
30 (329-510°C), for butenes, preferably from about 700°F to about 900°F (371-482°C), and  
31 about 350°F to about 650°F (177-343°C) for pentenes and hexenes. The pressure ranges  
32 from subatmospheric to about 200 psig, preferably from about 15 psig to about 200 psig,

1 and more preferably from about 1 psig to about 150 psig.

2       The liquid hourly space velocity during contacting is generally from about 0.1 to  
3 about 50 hr<sup>-1</sup>, based on the hydrocarbon feed, preferably from about 0.1 to about 20 hr<sup>-1</sup>,  
4 more preferably from about 0.2 to about 10 hr<sup>-1</sup>, most preferably from about 1 to about 5 hr<sup>-1</sup>.  
5       A hydrogen/hydrocarbon molar ratio is maintained from about 0 to about 30 or higher. The  
6 hydrogen can be added directly to the feed stream or directly to the isomerization zone. The  
7 reaction is preferably substantially free of water, typically less than about two weight  
8 percent based on the feed. The process can be carried out in a packed bed reactor, a fixed  
9 bed, fluidized bed reactor, or a moving bed reactor. The bed of the catalyst can move  
10 upward or downward. The mole percent conversion of, e.g., normal butene to iso-butene is  
11 at least 10, preferably at least 25, and more preferably at least 35.

#### Conversion of Paraffins to Aromatics

13       Catalytically active CIT-6 can be used to convert light gas C<sub>2</sub>-C<sub>6</sub> paraffins to higher  
14 molecular weight hydrocarbons including aromatic compounds. Preferably, the molecular  
15 sieve will contain a catalyst metal or metal oxide wherein said metal is selected from the  
16 group consisting of Groups IB, IIB, VIII and IIIA of the Periodic Table. Preferably, the  
17 metal is gallium, niobium, indium or zinc in the range of from about 0.05 to 5% by weight.

#### Xylene Isomerization

19       Catalytically active CIT-6 may also be useful in a process for isomerizing one or  
20 more xylene isomers in a C<sub>8</sub> aromatic feed to obtain ortho-, meta-, and para-xylene in a ratio  
21 approaching the equilibrium value. In particular, xylene isomerization is used in  
22 conjunction with a separate process to manufacture para-xylene. For example, a portion of  
23 the para-xylene in a mixed C<sub>8</sub> aromatics stream may be recovered by crystallization and  
24 centrifugation. The mother liquor from the crystallizer is then reacted under xylene  
25 isomerization conditions to restore ortho-, meta- and para-xylenes to a near equilibrium  
26 ratio. At the same time, part of the ethylbenzene in the mother liquor is converted to  
27 xylenes or to products which are easily separated by filtration. The isomerate is blended  
28 with fresh feed and the combined stream is distilled to remove heavy and light by-products.  
29       The resultant C<sub>8</sub> aromatics stream is then sent to the crystallizer to repeat the cycle.

30       Optionally, isomerization in the vapor phase is conducted in the presence of 3.0 to  
31 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene). If hydrogen is used,  
32 the catalyst should comprise about 0.1 to 2.0 wt.% of a hydrogenation/dehydrogenation

1 component selected from Group VIII (of the Periodic Table) metal component, especially  
2 platinum or nickel. By Group VIII metal component is meant the metals and their  
3 compounds such as oxides and sulfides.

4 Optionally, the isomerization feed may contain 10 to 90 wt.% of a diluent such as  
5 toluene, trimethylbenzene, naphthenes or paraffins.

6 Oligomerization

7 It is expected that catalytically active CIT-6 can also be used to oligomerize straight  
8 and branched chain olefins having from about 2 to 21 and preferably 2-5 carbon atoms. The  
9 oligomers which are the products of the process are medium to heavy olefins which are  
10 useful for both fuels, i.e., gasoline or a gasoline blending stock and chemicals.

11 The oligomerization process comprises contacting the olefin feedstock in the  
12 gaseous or liquid phase with a catalyst comprising catalytically active CIT-6.

13 The molecular sieve can have the original cations associated therewith replaced by a  
14 wide variety of other cations according to techniques well known in the art. Typical cations  
15 would include hydrogen, ammonium and metal cations including mixtures of the same. Of  
16 the replacing metallic cations, particular preference is given to cations of metals such as rare  
17 earth metals, manganese, calcium, as well as metals of Group II of the Periodic Table, e.g.,  
18 zinc, and Group VIII of the Periodic Table, e.g., nickel. One of the prime requisites is that  
19 the molecular sieve have a fairly low aromatization activity, i.e., in which the amount of  
20 aromatics produced is not more than about 20% by weight. This is accomplished by using a  
21 molecular sieve with controlled acid activity [alpha value] of from about 0.1 to about 120,  
22 preferably from about 0.1 to about 100, as measured by its ability to crack n-hexane.

23 Alpha values are defined by a standard test known in the art, e.g., as shown in U.S.  
24 Patent No. 3,960,978 issued on June 1, 1976 to Givens et al. which is incorporated totally  
25 herein by reference. If required, such molecular sieves may be obtained by steaming, by use  
26 in a conversion process or by any other method which may occur to one skilled in this art.

27 Condensation of Alcohols

28 Catalytically active CIT-6 can be used to condense lower aliphatic alcohols having 1  
29 to 10 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed  
30 aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent No. 3,894,107,  
31 issued July 8, 1975 to Butter et al., describes the process conditions used in this process,  
32 which patent is incorporated totally herein by reference.

The catalyst may be in the hydrogen form or may be base exchanged or impregnated to contain ammonium or a metal cation complement, preferably in the range of from about 0.05 to 5% by weight. The metal cations that may be present include any of the metals of the Groups I through VIII of the Periodic Table. However, in the case of Group IA metals, the cation content should in no case be so large as to effectively deactivate the catalyst, nor should the exchange be such as to eliminate all acidity. There may be other processes involving treatment of oxygenated substrates where a basic catalyst is desired.

## Other Uses for CIT-6

CIT-6 can also be used as an adsorbent with high selectivities based on molecular sieve behavior and also based upon preferential hydrocarbon packing within the pores.

11 CIT-6 is a hydrophobic material that can be used to remove some organic  
12 compounds from water.

13           CIT-6 may also be used for the catalytic reduction of the oxides of nitrogen in a gas  
14          stream. Typically, the gas stream also contains oxygen, often a stoichiometric excess  
15          thereof. Also, the CIT-6 may contain a metal or metal ions within or on it which are capable  
16          of catalyzing the reduction of the nitrogen oxides. Examples of such metals or metal ions  
17          include copper, cobalt and mixtures thereof.

18 One example of such a process for the catalytic reduction of oxides of nitrogen in the  
19 presence of a molecular sieve is disclosed in U.S. Patent No. 4,297,328, issued October 27,  
20 1981 to Ritscher et al., which is incorporated by reference herein. There, the catalytic  
21 process is the combustion of carbon monoxide and hydrocarbons and the catalytic reduction  
22 of the oxides of nitrogen contained in a gas stream, such as the exhaust gas from an internal  
23 combustion engine. The molecular sieve used is metal ion-exchanged, doped or loaded  
24 sufficiently so as to provide an effective amount of catalytic copper metal or copper ions  
25 within or on the molecular sieve. In addition, the process is conducted in an excess of  
26 oxidant, e.g., oxygen.

## Oxidation

28 Titanium-containing CIT-6 may be used as a catalyst in oxidation reactions.

29 The oxidizing agent employed in the oxidation processes of this invention is a  
30 hydrogen peroxide source such as hydrogen peroxide ( $H_2O_2$ ) or a hydrogen peroxide  
31 precursor (i.e., a compound which under the oxidation reaction conditions is capable of  
32 generating or liberating hydrogen peroxide).

1       The amount of hydrogen peroxide relative to the amount of substrate is not critical,  
2   but must be sufficient to cause oxidation of at least some of the substrate. Typically, the  
3   molar ratio of hydrogen peroxide to substrate is from about 100:1 to about 1:100, preferably  
4   10:1 to about 1:10. When the substrate is an olefin containing more than one carbon-carbon  
5   double bond, additional hydrogen peroxide may be required. Theoretically, one equivalent  
6   of hydrogen peroxide is required to oxidize one equivalent of a mono-unsaturated substrate,  
7   but it may be desirable to employ an excess of one reactant to optimize selectivity to the  
8   epoxide. In particular, the use of a moderate to large excess (e.g., 50 to 200%) of olefin  
9   relative to hydrogen peroxide may be advantageous for certain substrates.

10      If desired, a solvent may additionally be present during the oxidation reaction in  
11   order to dissolve the reactants other than the Ti-containing CIT-6, to provide better  
12   temperature control, or to favorably influence the oxidation rates and selectivities. The  
13   solvent, if present, may comprise from 1 to 99 weight percent of the total oxidation reaction  
14   mixture and is preferably selected such that it is a liquid at the oxidation reaction  
15   temperature. Organic compounds having boiling points at atmospheric pressure of from  
16   about 50°C to about 150°C are generally preferred for use. Excess hydrocarbon may serve  
17   as a solvent or diluent. Illustrative examples of other suitable solvents include, but are not  
18   limited to, ketones (e.g., acetone, methyl ethyl ketone, acetophenone), ethers (e.g.,  
19   tetrahydrofuran, butyl ether), nitriles (e.g., acetonitrile), aliphatic and aromatic  
20   hydrocarbons, halogenated hydrocarbons, and alcohols (e.g., methanol, ethanol, isopropyl  
21   alcohol, t-butyl alcohol, alpha-methyl benzyl alcohol, cyclohexanol). More than one type of  
22   solvent may be utilized. Water may also be employed as a solvent or diluent.

23      The reaction temperature is not critical, but should be sufficient to accomplish  
24   substantial conversion of the substrate within a reasonably short period of time. It is  
25   generally advantageous to carry out the reaction to achieve as high a hydrogen peroxide  
26   conversion as possible, preferably at least about 50%, more preferably at least about 90%,  
27   most preferably at least about 95%, consistent with reasonable selectivities. The optimum  
28   reaction temperature will be influenced by catalyst activity, substrate reactivity, reactant  
29   concentrations, and type of solvent employed, among other factors, but typically will be in a  
30   range of from about 0°C to about 150°C (more preferably from about 25°C to about 120°C).  
31   Reaction or residence times from about one minute to about 48 hours (more desirably from  
32   about ten minutes to about eight hours) will typically be appropriate, depending upon the

1 above-identified variables. Although subatmospheric pressures can be employed, the  
2 reaction is preferably performed at atmospheric or at elevated pressure (typically, between  
3 one and 100 atmospheres), especially when the boiling point of the substrate is below the  
4 oxidation reaction temperature. Generally, it is desirable to pressurize the reaction vessel  
5 sufficiently to maintain the reaction components as a liquid phase mixture. Most (over  
6 50%) of the substrate should preferably be present in the liquid phase.

7 The oxidation process of this invention may be carried out in a batch, continuous, or  
8 semi-continuous manner using any appropriate type of reaction vessel or apparatus such as a  
9 fixed bed, transport bed, fluidized bed, stirred slurry, or CSTR reactor. The reactants may  
10 be combined all at once or sequentially. For example, the hydrogen peroxide or hydrogen  
11 peroxide precursor may be added incrementally to the reaction zone. The hydrogen  
12 peroxide could also be generated in situ within the same reactor zone where oxidation is  
13 taking place.

14 Once the oxidation has been carried out to the desired degree of conversion, the  
15 oxidized product may be separated and recovered from the reaction mixture using any  
16 appropriate technique such as fractional distillation, extractive distillation, liquid-liquid  
17 extraction, crystallization, or the like.

18 Additional details for oxidation reactions are disclosed in U. S. Patent No.  
19 5,869,706, issued February 9, 1999 to Dartt and Davis, which is incorporated herein by  
20 reference in its entirety.

21 Vanadium-containing CIT-6 may be used as a catalyst in the  
22 oxidation/dehydrogenation of hydrocarbons. For example, vanadium-containing CIT-6 may  
23 be used to partially (or completely) oxidize hydrocarbons in the presence of oxygen (air) or  
24 hydrogen peroxide. The oxidation may either be complete, i.e., oxidizing the hydrocarbon  
25 to carbon dioxide, or partial, as in the oxidation of propane to propylene. The reaction is  
26 conducted under conditions that yield the desired degree of oxidation, and are known in the  
27 art.

28 EXAMPLES

29 The following examples demonstrate but do not limit the present invention.

30 Example 1-25

31 Synthesis of Zn-CIT-6

32 Zn-CIT-6 reaction mixtures are prepared by the following method. After the organic

1 and inorganic cations are dissolved in distilled water, zinc acetate dihydrate is added. Next,  
2 silica is added and the mixture is stirred for two hours.

3 The starting mixtures are each charged into Teflon-lined, stainless autoclaves and  
4 heated statically in convection ovens. The products are collected by vacuum filtration,  
5 washed with distilled water, and dried in air at room temperature. In order to remove the  
6 occluded organic molecules, the product is heated in air to 540°C within six hours and  
7 maintained at this temperature for six hours. An as-made Zn-CIT-6 is treated with 1 M  
8 aqueous ammonium nitrate solution at 80°C for ten hours. The treated sample is recovered  
9 by vacuum filtration and washed with distilled water. This procedure is repeated four times.  
10 The final material is dried in air at room temperature.

11 Using the above procedure, the products indicated below are made from a reaction  
12 mixture having the following composition:



14

*To v. mlch*

Example No.	b	c	a	D	Temp. (°C)	Days	Product
1	0.05	0.55	0.03	30	150	3	CIT-6
2	0.05	0.55	0.03	30	150	5	CIT-6 + VPI-8
3	0.05	0.55	0.03	30	150	7	VPI-8
4	0.2	0.4	0.03	30	150	3	VPI-8
5	0.05	0.55	0.03	30	175	2	Amorph.
6	0.05	0.55	0.03	30	175	3	VPI-8
7	0.05	0.55	0.03	30	135	9	CIT-6
8	0.05	0.55	0.03	30	135	15	CIT-6
9	0.05	0.55	0.03	30	135	18	VPI-8
10	0.05	0.45	0.03	30	150	6	VPI-8
11	0.05	0.55	0.03	30	150	4	CIT-6
12	0.05	0.55	0.03	30	150	6	VPI-8
13	0.05	0.6	0.03	30	150	4	CIT-6
14	0.05	0.6	0.03	30	150	29	VPI-8 +

							small amnt. CIT-6
15	0.05	0.65	0.03	30	150	4	CIT-6
16	0.05	0.65	0.03	30	150	17	CIT-6 + small amnt. VPI-8
17	0.05	0.65	0.03	40	150	4	CIT-6
18	0.05 <sup>1</sup>	0.65	0.03	30	150	14	Amorph.
19	0.05	0.6	0.01	30	150	11	Amorph. + small amnt. MFI
20	0.05	0.6	0.01	30	150	18	MFI
21	0.05	0.55	-	30	150	5	MTW
22	0.05	0.65	0.05	30	150	4	CIT-6 + small amnt. VPI-8
23	0.02	0.6	0.03	30	150	17	Amorph.
24	0.1	0.6	0.03	30	150	4	Unknown + CIT-6
25 <sup>2,3</sup>	0.05	0.7	0.03	30	150	4	CIT-6

1

2      <sup>1</sup>NaOH used instead of LiOH.3      <sup>2</sup>Silica source is Cab-O-Sil M5 fumed silica. All others are HS-30.4      <sup>3</sup>Milky white mixture heated at 80°C for three hours to get a clear solution.

5

6      The results above demonstrate that (1) too long a reaction time can produce VPI-8

7      instead of Zn-CIT-6 (Ex. 3,9, 12, 14 and 17); (2) too high a reaction temperature may not

1 produce Zn-CIT-6 (Ex. 5 and 6); (3) the presence and concentration of lithium is critical to  
2 formation of Zn-CIT-6 (Ex. 4, 18 and 22); and the presence and concentration of zinc is  
3 critical to formation of Zn-CIT-6 (Ex. 19, 20 and 21).

4                   Example 26

5                   Synthesis of Zincoaluminosilicate CIT-6

6                   A solution of tetraethylammonium hydroxide (4.10 grams of a 35 wt.% solution) is  
7 added to 3.34 grams of water. To this is added 0.018 gram of LiOH, 0.098 gram of zinc  
8 acetate dihydrate, and 0.056 gram of  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  and the resulting mixture stirred.  
--- 9 Three grams of Ludox HS-30 silica is added and the resulting mixture stirred for two hours.  
10 The resulting solution is charged into a Teflon-lined autoclave, and heated (statically) at  
11 150°C for four days. The product was CIT-6 containing both zinc and aluminum in the  
12 crystal framework.

13                   Example 27

14                   Extraction of TEA and Zinc

15 The TEA and zinc are extracted from the CIT-6 prepared in Example 26 by contacting 0.1  
16 gram of the aluminozincosilicate CIT-6 with a solution containing 6 ml acetic acid, 1 ml  
17 pyridine and 10 ml water at 135°C for two days. The TEA and zinc are extracted from the  
18 CIT-6, but the aluminum remains in the crystal framework, as shown by  $^{27}\text{Al}$  NMR.

19                   Example 28

20                   Cyclohexane Adsorption

21 The adsorption amount of vapor-phase cyclohexane (99.5%, EM) for Zn-CIT-6 is measured  
22 at 25°C using a McBaine-Bakr balance. Prior to the adsorption experiment, calcined  
23 samples of CIT-6 are dehydrated at 350°C under vacuum for five hours. The saturation  
24 pressure,  $P_0$ , of cyclohexane is 97.5 mm Hg. The adsorption is performed at a cyclohexane  
25 pressure of 30 mm Hg. The amount of adsorbed cyclohexane of the Zn-CIT-6 sample is  
26 0.16 ml/g. This value is slightly smaller than that of aluminosilicate beta (0.22 ml/g).

27                   Example 29

28                   Extraction of TEA and Zinc

29 The TEA and zinc are extracted from Zn-CIT-6 by contacting 0.1 gram of CIT-6  
30 with a solution containing 6 ml acetic acid, 0.1 ml pyridine and 10 ml water at 60°C for  
31 three days.

### Example 30

### Insertion of Aluminum

3           Aluminum is inserted into the product of Example 29 by contacting the product with  
4       an aqueous solution of aluminum nitrate at a 1 : 2 : 50 weight ratio of Zn-CIT-6 : aluminum  
5       nitrate : water at 80°C for one day.

### Example 31

## Insertion of Titanium

8           Titanium is inserted into the product of Example 29 by contacting the product with  
9   1.5 ml 1M  $TiCl_4$  toluene solution and 10 ml toluene at 80°C for 12 hours under nitrogen  
10   atmosphere. After treatment, the sample is filtrated, washed with acetone and dried. UV  
11   analysis of the resultant product shows that titanium is inserted in the product.

### Example 32

### Preparation of Pd-Zn-CIT-6

14           2.84 grams of Zn-CIT-6 synthesized as in Example 1 is calcined to 540°C in a  
15 mixture of air and nitrogen, and subsequently ion-exchanged once with ammonium nitrate at  
16 85°C for two hours, recovered and dried to 300°C. Pd acetylacetone ( 0.0286 gms) in  
17 toluene ( 2.25 ml) is admitted into a sealed bottle in which the heated Zn-CIT-6 has been  
18 placed. This provides for some vacuum at room temperature. The bottle is manually shaken  
19 while the solution is admitted by syringe. The wetted solid is allowed to stand overnight.  
20 Next the material is calcined to 425°C in air.  
21

### Example 33

### Catalytic Activity

The Pd-Zn-CIT-6 prepared in Example 30 is loaded as 24-40 mesh particles into a stainless steel reactor. 0.50 Gram is packed into a 3/8 inch stainless steel tube with alundum on both sides of the zeolite bed. A Lindburg furnace is used to heat the reactor tube. Helium is introduced into the reactor tube at 10 cc/min. and at atmospheric pressure. The reactor is heated to about 372°C, and a 50/50 (w/w) feed of n-hexane and 3-methylpentane is introduced into the reactor at a rate of 8 µl/min. Feed delivery is made via a Brownlee pump. Direct sampling into a gas chromatograph begins after 10 minutes of feed introduction. At 800°F (427°C) and 10 minutes on stream the catalyst gives 47% conversion with the products being about 1/3 aromatics, 1/3 isomerized C<sub>6</sub> and a third olefins from

1 dehydrogenation. There is a few percent cracked product. There is no preference for reaction  
2 of either isomer.

3                   Example 34

4                   Synthesis of All-Si CIT-6 From All-silica Mesoporous Material

5       MCM-41 is prepared using the following gel composition where C<sub>16</sub>TMA is  
6 hexadecyltrimethylammonium:



8       The gel is placed in an autoclave at 120°C for three days. The resulting MCM-41 crystals  
9       are recovered and calcined at 540°C for ten hours.

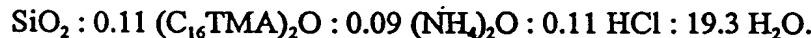
10      The calcined MCM-41 (0.1 gram) is impregnated with 0.3 gram of 35 wt.% TEAOH  
11     aqueous solution and dried at room temperature for one day (TEAOH/Si = 0.4, H<sub>2</sub>O/Si =  
12     ~2). The resulting powder is charged into an autoclave and heated at 150°C for seven days.  
13      The product is all-silica zeolite beta.

14      0.1 Gram of the all-silica zeolite beta (still containing TEAOH) is treated with a  
15     mixture of 6 ml acetic acid and 10 ml water at 135°C for two days. Almost all of the  
16     TEAOH is removed from the material, and it retains the beta zeolite structure. The resulting  
17     product is highly hydrophobic.

18                   Example 35

19                   Synthesis of Si-MCM-41

20      Si-MCM-41 materials (Si-1-MCM-41) are prepared by adding 2.4 grams of 29 wt.%  
21     NH<sub>4</sub>OH solution (EM) to 26.4 grams of 29 wt.% hexadecyltrimethylammonium chloride  
22     (C<sub>16</sub>TMACl) solution. This solution is combined with 2.3 grams of tetramethylammonium  
23     hydroxide pentahydrate (TMAOH·5H<sub>2</sub>O), 20 grams of tetramethylammonium silicate (10  
24     wt.% SiO<sub>2</sub>, TMA/Si = 0.5) and 4.5 grams of fumed silica (Cab-O-Sil M-5 from Cabot)  
25     under stirring. The composition of the resulting gel is:



27      The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated  
28     statically at 140°C for three days. The product is collected by vacuum filtration, washed  
29     with water and dried in air at room temperature. In order to remove occluded molecules, the  
30     as-made sample is calcined in air at 550°C within six hours and maintained at this  
31     temperature for six hours. The product is identified as MCM-41 and designated Si-1-MCM-  
32     41.

### Example 36

## Synthesis of Si-MCM-41

3 Concentrated H<sub>2</sub>SO<sub>4</sub> (1.2 grams) is added dropwise to 20 grams of sodium silicate (10.8  
4 wt.% Na<sub>2</sub>O, 27.0 wt.% SiO<sub>2</sub> and 62.2 wt.% H<sub>2</sub>O) in 42.8 grams of water under stirring.  
5 Next, 16.8 grams of C<sub>16</sub>TMABr in 50.3 grams of water is added to the solution and the  
6 resulting mixture is stirred for two hours. The resulting gel has the composition:



8 The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated  
9 statically at 120°C for three days. The product is collected by vacuum filtration, washed  
10 with water and dried in air at room temperature and calcined in air at 550°C within six hours  
11 and maintained at this temperature for six hours to remove the organic molecules. The  
12 organic molecules occluded in the pores of the material are also removed by contacting the  
13 as-made sample with 1M HCl solution in diethyl ether at room temperature. The product is  
14 identified as MCM-41 and designated Si-2-MCM-41.

### Example 37

## Synthesis of MCM-48

17           NaOH (0.8 gram) is dissolved in 44 grams of water. To this solution is added 8.89  
18        grams of C<sub>16</sub>TMABr and finally 8.33 grams of TEOS is added to it. The resulting mixture is  
19        stirred at room temperature for two hours. The mixture has the following composition:



21 The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated  
22 statically at 105°C for three days. The product is collected by vacuum filtration, washed  
23 with water and dried in air at room temperature and calcined in air at 550°C within six hours  
24 and maintained at this temperature for six hours to remove the organic molecules. The  
25 product is identified as MCM-48.

### Example 38

## Synthesis of Al-Containing MCM-41

28        2.4 Grams of 29 wt.% NH<sub>4</sub>OH solution is added to 26.4 grams of 29 wt.%  
29        C<sub>16</sub>TMACl solution. To this, 0.37 gram of sodium aluminate (54 wt.% Al<sub>2</sub>O<sub>3</sub>, 41 wt.%  
30        Na<sub>2</sub>O, 5 wt.% H<sub>2</sub>O) is added and the solution is combined with 2.3 grams of TMAOH·5H<sub>2</sub>O,  
31        20 grams of tetramethylammonium silicate (10 wt.% SiO<sub>2</sub>, TMA/Si = 0.5) and 4.5 grams of  
32        fumed silica (Cab-O-Sil M-5) under stirring. The resulting gel composition is:

1  $\text{SiO}_2$  : 0.02  $\text{Al}_2\text{O}_3$  : 0.02  $\text{Na}_2\text{O}$  : 0.11  $(\text{C}_{16}\text{TMA})_2\text{O}$  : 0.13  $(\text{TMA})_2\text{O}$  : 0.09  $(\text{NH}_4)_2\text{O}$  : 0.22  
2  $\text{HCl}$  : 19.3  $\text{H}_2\text{O}$ .  
3 The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated  
4 statically at 135°C for three days. The product is collected by vacuum filtration, washed  
5 with water and dried in air at room temperature. In order to remove the occluded molecules,  
6 the as-made sample is calcined in air at 550°C within six hours and maintained at this  
7 temperature for six hours. The product is identified as MCM-41 containing aluminum in its  
8 framework, and is designated Al-MCM-41.

### Example 39

## Synthesis of B-Containing MCM-41

11 A mixture of 1 gram of fumed silica (Cab-O-Sil M5) and 6.4 grams of water are  
12 mixed under vigorous stirring. After ten minutes of mixing, a solution of 3.3 grams of  
13 C<sub>16</sub>TMABr in 21.7 grams of water is added to this slurry. After another ten minutes of  
14 stirring, a third solution containing 2.9 grams of tetramethylammonium silicate solution (10  
15 wt.% SiO<sub>2</sub>, TMA/Si = 0.5) and 1.4 grams of sodium silicate is added to the slurry. H<sub>3</sub>BO<sub>3</sub>  
16 (0.034 gram) is added and the mixing continued for 30 minutes. The resulting gel has the  
17 composition:

$\text{SiO}_2$  : 0.02  $\text{H}_3\text{BO}_3$  : 0.16  $\text{C}_{16}$  TMABr : 0.085  $\text{Na}_2\text{O}$  : 63  $\text{H}_2\text{O}$ .

19 The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated  
20 statically at 100°C for one day. The product is collected by vacuum filtration, washed with  
21 water and dried in air at room temperature and calcined under nitrogen for temperatures up  
22 to 550°C within six hours and maintained at this temperature for two hours before slowly  
23 switching from nitrogen to air. After an additional four hours at 500°C, the sample is cooled  
24 to room temperature. The product is identified as MCM-41 containing boron in its  
25 framework, and is designated B-MCM-41.

### Example 40

## Synthesis of V-Containing MCM-41

28        6.24 Grams of tetraethyl orthosilicate (TEOS), 0.16 gram of vanadyl acetylacetone,  
29        9 grams of ethanol, and 1.8 of isopropyl alcohol are mixed together (Solution A). A second  
30        solution (B) contains 1.5 grams of dodecylamine ( $C_{12}A$ ), 0.6 gram of 1 N HCl and 19 grams  
31        of water. Solution A is added slowly to Solution B under vigorous stirring. The resulting  
32        reaction mixture has the following composition:

1            $\text{SiO}_2$  : 0.02    $\text{VO}(\text{acac})_2$  : 0.27    $\text{C}_{12}\text{A}$  : 0.02    $\text{HCl}$  : 36    $\text{H}_2\text{O}$  : 10.5    $\text{EtOH}$  : 1    $\text{iPrOH}$ .  
2       The mixture is stirred at room temperature for 12 hours. The product is collected by  
3       vacuum filtration, washed with water and dried in air at room temperature and calcined in  
4       air at 550°C within six hours and maintained at this temperature for six hours to remove  
5       organic molecules. The product is identified as MCM-41 containing vanadium in its  
6       framework, and is designated V-MCM-41.

7                                  Example 41

8                                  Synthesis of Zr-Containing MCM-41

9       Solution A is prepared by mixing 10.42 grams of TEOS, 0.47 gram of zirconium  
10      propoxide (70 wt.% solution in 1-propanol). A second solution (B) contains 4 grams of  
11      octadecylamine ( $\text{C}_{18}\text{A}$ ), 15 grams of ethanol and 27 grams of water. Solution A is added  
12      slowly to Solution B under vigorous stirring. The resulting reaction mixture has the  
13      following composition:



15       The mixture is stirred at room temperature for 12 hours. The product is collected by  
16       vacuum filtration, washed with water and dried in air at room temperature and calcined in  
17       air at 550°C within six hours and maintained at this temperature for six hours to remove  
18       organic molecules. The product is identified as MCM-41 containing zirconium in its  
19       framework, and is designated Zr-MCM-41.

20                                  Example 42

21                                  Synthesis of Zn-Containing MCM-41

22       0.18 Gram of zinc acetate dihydrate ( $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ) and 0.8 gram of NaOH are  
23       dissolved in 44 grams of water. 8.89 Grams of  $\text{C}_{16}\text{TMABr}$  is added to this solution and  
24       finally 8.33 grams of TEOS is added. The resulting mixture is stirred at room temperature  
25       for two hours. The reaction mixture has the following composition:



27       The reaction mixture was charged into a Teflon-line, stainless steel autoclave and heated  
28       statically at 105°C for three days. The product is collected by vacuum filtration, washed  
29       with water and dried in air at room temperature and calcined in air at 550°C within six hours  
30       and maintained at this temperature for six hours to remove organic molecules. The product  
31       is identified as MCM-41 containing zinc in its framework, and is designated Zn-MCM-41.

1                   Examples 43-49

2                   Synthesis of CIT-6 from Mesoporous Materials

3                   Calcined, mesoporous materials are each in turn impregnated with 35 wt.% TEAOH  
4                   aqueous solution and dried at room temperature for 12 hours. The resulting powder is  
5                   charged into a Teflon-lined autoclave and heated at 150°C statically. The product is washed  
6                   with distilled water and dried in air at room temperature. In order to remove the occluded  
7                   molecules, the as-made sample is calcined in air at 550°C within six hours and maintained at  
8                   this temperature for six hours. The organic molecules occluded in the pores of the as-made  
9                   sample are also removed by contacting the as-made sample with acetic acid at 135°C for two  
10                  days.

11                  A typical procedure is as follows: 0.1 gram of calcined Si-MCM-41 is impregnated  
12                  with 0.3 gram of 35 wt.% TEAOH aqueous solution (TEAOH/Si = 0.4) and dried at room  
13                  temperature for 12 hours ( $H_2O/SiO_2$  molar ratio is about 1.5). The resulting powder is  
14                  heated at 150°C for one week in an autoclave. The yield of crystalline solid after calcination  
15                  is about 80%. Conditions for specific materials are shown in the table below.

16

Example Number	Non-Si Atom Containing Mesoporous Material <sup>(a)</sup>	Impregnated TEAOH/Si Ratio	Conditions	Result <sup>(a)</sup>
43	Al-MCM-41 (26)	0.4	150°C x 7 days	Al-Beta (26)
44	B-MCM-41 (54)	0.4	150°C x 7 days	B-Beta (62)
45	Ti-MCM-41 (47)	0.4	150°C x 7 days	Ti-Beta (47)
46	Si-MCM-41	0.4 + Ti (0.02)	150°C x 7 days	Si-Beta (63)
47	V-MCM-41 (59)	0.4	150°C x 7 days	V-Beta (148)
48	Zr-MCM-41 (47)	0.4	150°C x 7 days	Zr-Beta (73)
49	Zn-MCM-41	0.4	150°C x 7 days	Zn-Beta (30)

1  
2     (a) Values in parentheses are the Si/Y molar ratios (Y = Al, B, Ti, V, Zr or Zn) in the as-  
3     made product, measured by elemental analysis.

4  
5     The as-made materials are then calcined to remove the TEA cations.

6                         Example 50

7                         Synthesis of Ti-Containing CIT-6

8     Calcined Si-MCM-41 is impregnated with a solution containing titanium  
9     tetraisopropoxide ( $Ti/Si = 0.02$ ) and a 35 wt.% aqueous solution of TEAOH ( $TEA/Si = 0.4$ ).  
10    The impregnated solid is treated as described above in Examples 43-49. The resulting  
11    product is CIT-6 containing titanium in its framework.

12    The results above clearly indicate that a highly crystalline all-Si-CIT-6 is formed  
13    from Si-MCM-41 using TEAOH as the organic template (or structure directing agent).  
14    When  $Na^+$  was added to the reaction mixture, it was found that all-Si-CIT-6 is formed faster  
15    than in the absence of  $Na^+$ . It was also found that when fumed silica was used as the silica  
16    source, only amorphous phases were obtained, even if  $Na^+$  is added. Conventional  
17    hydrothermal reaction ( $H_2O/Si = 20$ ) yields only amorphous products as well. When using  
18    MCM-48 as a silica source, all-Si-CIT-6 is also formed. These data indicate that  
19    mesoporous silicas such as MCM-41 and MCM-48 can be used to synthesize all-Si-CIT-6,  
20    that  $Na^+$  cations promote the conversion to all-Si-CIT-6 and that the mesoporous materials  
21    can also be used to prepare CIT-6.